

The Reactions of Carbon Atoms
with N_2 , H_2 , and D_2 at $4.2^\circ K$.

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The reactions of carbon atoms with various molecules have been the subject of several studies in the gas and solid phases.^{1,2,3} Jacox et al.³ have recently observed the reaction of C with CO to give the CCO radical in matrices of Ar and N_2 at $14^\circ K$ using the ultraviolet photolysis of cyanogen azide as a source of carbon atoms.

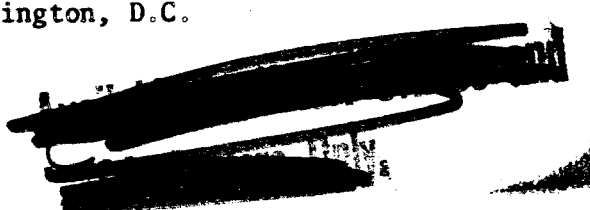
The high reactivity of atomic carbon towards stable molecules qualifies it for many reactions leading to unstable intermediates of fundamental interest. Using the matrix isolation technique to stabilize these intermediates, reaction mechanisms and structures can be determined. We discuss here the results of some studies using carbon suboxide, C_3O_2 , as a photolytic source of C atoms and N_2 , H_2 , and D_2 as reactants.

Carbon suboxide was synthesized by heating a mixture of phosphorus pentoxide and malonic acid in 10:1 weight ratio under vacuum to $140^\circ C$, collected in a cold trap at $77^\circ K$, and purified by repeated bulb-to-bulb distillations. Ar, N_2 , H_2 and D_2 of high commercial grade were purified by passing over copper at $500^\circ C$ and through a liquid N_2 trap.

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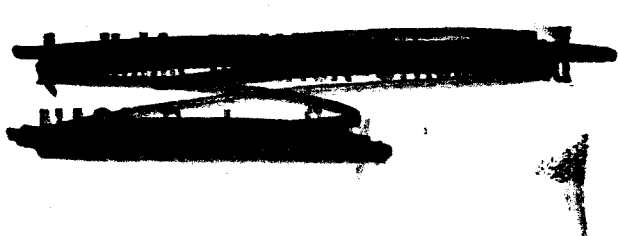


The cryostat used is similar to one described by Schoen et al.⁴ for optical studies at low temperatures. The cold window was cooled to 4.2°K with liquid He. Infrared absorption spectra were recorded with Beckman IR-7 and IR-11 spectrometers and calibrated with standard gases.

Photolyses were conducted with low pressure xenon resonance lamps⁵ equipped with LiF windows which transmit the Xe resonance lines above 1050Å.

Photodecomposition of carbon suboxide in a matrix of N₂ gives rise to new absorptions at 2858, 2165, 2128, 1478, 1252, 423, and 394 cm⁻¹ in addition to the CO and CCO absorptions previously observed when C₃O₂ was irradiated in an Ar matrix.³ The frequencies and intensity ratios of the 1478 and 423 cm⁻¹ bands match those observed for the NCN radical in a nitrogen matrix by Milligan et al.^{6,7} on photolysis of N₃CN. The appearance of these absorptions characteristic of NCN in the N₂:C₃O₂ system is strong evidence that carbon atom insertion into the N₂ triple bond is occurring in these experiments. The 1252 and 394 cm⁻¹ bands, also observed by Milligan et al., may be due to CNN. Evidences for the existence of this species have been obtained in other studies.^{8,9} It has been suggested³ that the features at 2165 and 2128 cm⁻¹ may be due to the species CCO, although it should be pointed out that these bands appear upon photolysis of C₃O₂ in nitrogen but not in argon matrices.

Previous photolytic studies in the gas phase¹⁰ and in matrices^{11,12} have demonstrated the extraordinary reactivity of methylene, CH₂. This reactivity has prevented the stabilization of methylene in quantities sufficient for infrared observation. Because carbon atoms react with H₂ to give CH₄ and other products in the gas phase¹³ with methylene as a proposed intermediate, the photodecomposition of carbon suboxide in an argon matrix containing H₂ or D₂



seemed to be a feasible technique for the formation and stabilization of an observable amount of methylene.

Good evidence for the generation and ensuing reaction of CH_2 was obtained in experiments utilizing this technique, but no direct infrared observation of the species was made. In all experiments the initial C_3O_2 concentration was between 0.25 and 1.0 mole per cent while the concentration of H_2 or D_2 was varied from 0.5 to 16%. At H_2 concentrations less than 4% the predominant reaction product was ketene, presumably formed by the reaction of CH_2 with CO ¹⁴ present from the C_3O_2 decomposition. The reaction of CCO with H_2 to form ketene can not be excluded in this system. At higher H_2 concentrations the reaction of methylene with H_2 to give CH_4 also occurred.^{10,15} Absorption frequencies (in cm^{-1}) of CH_2CO (3066, 2143, 1381), CD_2CO (~2260, 2149, 2113, 848), CH_4 (3040-3010, 1306), and CD_4 (994) observed here agree well with the more intense matrix absorptions previously observed for these molecules.^{16,17} CH_4 and CD_4 showed no rotational fine structure, possibly because of the heterogeneous nature of the matrix.

In an experiment in which both H_2 and D_2 were present in the matrix all the above absorption features were obtained as well as weaker features near 1030 and 1235 cm^{-1} probably arising from CH_2D_2 .

Broad absorptions from 730 to 750 cm^{-1} and from 3265 to 3275 cm^{-1} occurring weakly after photolysis of $\text{Ar:H}_2:\text{C}_3\text{O}_2$ mixtures containing more than 5% H_2 have been assigned to acetylene. Positive identification of C_2D_2 was not possible in experiments with $\text{Ar:D}_2:\text{C}_3\text{O}_2$ mixtures because of an intense C_3O_2 absorption near 539 cm^{-1} where the stronger of the C_2D_2 bands should have occurred. Several reaction sequences leading to acetylene formation might be proposed but the most likely is the insertion of carbon atoms into C-H bonds in methane or ketene followed by cleavage to give acetylene.^{18,19}

Absorption bands observed at 1861 and 1086 cm^{-1} are attributed to HCO^{20,21}. Corresponding features of DCO were not observed with certainty.

An absorption at 2018 cm^{-1} with a deuterium isotopic counterpart at 1990 cm^{-1} was observed which grew on photolysis and seemed to decrease when the matrix was warmed sufficiently for diffusion to occur. This feature has not been identified. In the experiment using a mixture of H_2 and D_2 no new features were observed between 1990 and 2018 cm^{-1} , indicating that the species contains no more than two hydrogen atoms. Strong absorption in this spectral region is characteristic of molecules containing the C=C=O group.

In the light of the small size and great reactivity of methylene it is perhaps not surprising that appreciable amounts of the species were not stabilized. Near the site where each methylene was formed, there were two molecules of CO and possibly also H_2 with which CH_2 could react.

These experiments have given further evidence of the great reactivity of carbon atoms. By means of the matrix isolation technique it has been possible to study the reaction of carbon atoms with nitrogen and hydrogen molecules, to trap and observe unstable intermediates, including NCN, and to generate methylene for further studies of its reactivity.

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